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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Chemical and electrochemical studies were carried out in ambient temperature chloroaluminum molten salts composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride. Simultaneous electrochemical in EPR work was performed on polypyrrole and polyfluorene in the molten salts. The chemistry and electrochemistry of a number of solutes, benzoquinone, several molybdenum dimers, and ferro/ferricyanide, were examined. ²⁷ O NMR spectroscopy was employed to assess the behavior of oxide in the molten salts. Gutmann donor-acceptor numbers were obtained making use of electrochemical and NMR, ³¹ P, measurements. A new molten salt, 1-ethyl-3-methylimidazolium hydrogen dichloride, was prepared. It was found that EtAlCl ₂ could be employed to quantitatively remove protons from the melts. Ultramicroelectrode studies were carried out in both molten salt and in aqueous media, the latter work to assess their capabilities relevant to our studies.				
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This is a Final Report on AFOSR 87-0088, Chemical and Electrochemical Studies in Ionic Liquids.

The research carried out under this grant involved studies of the chemistry and electrochemistry of ambient temperature chloroaluminate ionic liquids. The ionic liquids consist of mixtures of an organic chloride, 1-methyl-3-ethylimidazolium chloride, with aluminum chloride.

This activity was funded under a three-year option grant as of December 1, 1986, and expired November 30, 1989. Funding levels were \$160,597 (FY 1987), \$128,935 (FY 1988), and \$131,440 (FY 1989).

This Final Report discusses topics as submitted in our proposal in this area. In the interest of brevity, abstracts or summaries of work published will be used. All publications under this, and prior, AFOSR support are listed in Appendix A, as are listings of formal meeting presentations. Three manuscripts, A-69, A-80 and A-81, in press at the time of the prior Final Report on AFOSR-84-0292, and discussed therein, were published during the duration of this grant and citations have been up-dated.

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SUMMARY OF WORK: 1 DECEMBER, 1986 - 30 NOVEMBER, 1989

I. COMPLETED WORK

**A. STUDIES OF MODIFIED ELECTRODES IN AMBIENT TEMPERATURE
MOLTEN SALTS**

Here we report on a number of studies of polymer coated electrodes in the ambient temperature ionic liquids.

1 Simultaneous EPR-Electrochemistry on Polypyrrole

A manuscript, "Simultaneous EPR Electrochemical and Spectroscopic Studies in Ambient Temperature Ionic Liquids", has been published in the Journal of Electroanalytical and Interfacial Chemistry. See Appendix A, Ref. 87.

ABSTRACT

EPR, current and charge measurements have been made simultaneously (a) vs potential during linear scan experiments and (b) vs time during chronoamperometric experiments on a polypyrrole film in an ambient temperature molten salt consisting of 1-methyl-3-ethylimidazolium chloride + aluminum chloride. The linear scan experiments show an EPR absorption over a very narrow potential region, about 200 mV, and a strong correlation between the maximum EPR absorption and the peak current. Chronoamperometric experiments show that equilibrium is achieved after 10-15 s and that the paramagnetic species (radical cation) is necessarily an intermediate in the process of switching the film from its neutral to fully oxidized state, or the reverse. The characteristics of the EPR signal are reported.

2. Electropolymerization of Fluorene

A manuscript entitled "Investigations on the Formation of Polyfluorene and Its Electrochemistry in Ambient Temperature Ionic Liquids", was published in the Journal of the Electrochemical Society. See Appendix A, Ref. 85.

ABSTRACT

Polyfluorene films were deposited on platinum, tungsten, and glassy carbon electrodes by the anodic oxidation of the monomer in ambient temperature molten salts consisting of a mixture of aluminum chloride and 1-methyl-3-ethylimidazolium chloride. The polymer films are conductive in the oxidized state and nonconductive when reduced. The collection efficiency measured by rotating ring-disk voltammetry in neutral melts suggests that two protons per monomer are released during the polymerization process for both polyfluorene and polypyrrole formation. The polyfluorene films obtained in these molten salts are

more stable and their electrochemical behavior less complicated than those prepared in acetonitrile.

3. Simultaneous EPR-Electrochemistry on Polyfluorene

A manuscript, "Simultaneous EPR Electrochemical Measurements on Polyfluorene in Ambient Temperature Ionic Liquids", was published in Synthetic Metals. See Appendix A, Ref. 88.

ABSTRACT

Simultaneous electron paramagnetic resonance (EPR) and electrochemical measurements have been carried out on polyfluorene prepared by monomer oxidation and utilized in an ambient temperature ionic liquid consisting of 1-methyl-3-ethylimidazolium chloride-aluminum chloride. A considerable EPR signal is observed in both the reduced and oxidized states; the EPR signal achieves a maximum value coincident with the peak current during a cyclic voltammogram. Assuming that the process is two one-electron steps, initially forming a radical cation, the difference between the two E^0 values is estimated as less than 70 mV.

4. (Phenyl)₃Si

This material was successfully polymerized in the acidic $AlCl_3$ - $ImCl$ molten salt, and shows electroactivity. ESCA indicates that, perhaps, the Im^+ cation is incorporated into the film. Although additional work is desirable, it will not be done. However, a manuscript on what has been done may be prepared (R. Carlin and R.A. Osteryoung, unpublished).

5. Anthraquinone Containing Polymer

We prepared [1-(pyrrol-1-yl)-hex-6-yl]-9,10-anthraquinone-2-sulfonate (PHAS). The monomer was characterized by NMR and IR, and showed typical anthraquinone behavior in the molten salts. It could be polymerized, but though the polymer showed electrochemical behavior typical of polypyrrole, no anthraquinone electrochemistry could be seen (B. Das and R. A. Osteryoung, unpublished). At this time, this activity has been abandoned.

B. ELECTROCHEMICAL STUDIES

1. Study of Benzoquinone

A manuscript, "Electrochemical and Spectroscopic Studies of 1,4-Benzoquinone in Ambient Temperature Chloroaluminate Molten Salts", has been published in the Journal of the Electrochemical Society. See Appendix A, Ref. 86.

ABSTRACT

The chemical, electrochemical, and spectroscopic properties of

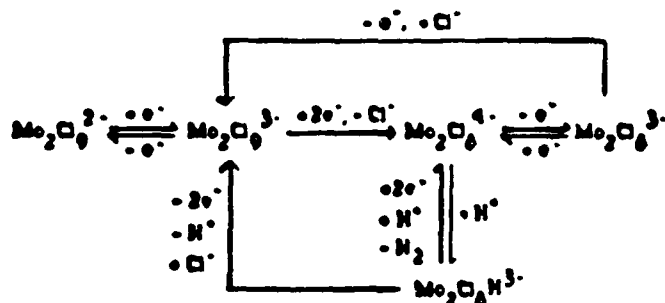
1,4-benzoquinone (Q) have been studied in the aluminum chloride:1-methyl-3-ethylimidazolium chloride (ImCl) ionic liquid. In basic melts ($\text{AlCl}_3:\text{ImCl}$ mole ratio < 1.0), fast scan voltammetry (up to 1000 V s^{-1}) shows that Q reduces to Q^{2-} in a fast two-electron step, probably followed by solvation of the dianion. Infrared and visible spectroscopic data, and electrochemical measurements, show that Q reacts with Cl^- in basic melts producing the dianion of monochlorhydroquinone. Q shows no electrochemical response in acidic melts (1.2:1 $\text{AlCl}_3:\text{ImCl}$). However, it reacts with the solvent and eventually generates HCl which is electrochemically detected at a Pt electrode. The corresponding IR spectrum of the solution lacks the major absorption band in the vicinity of 1657 cm^{-1} , while the $\text{C}=\text{O}$ stretching band is observed for Q in neutral or basic melts. When the acidic melt is neutralized and made basic by the addition of ImCl, the cyclic voltammogram shows no presence of Q, which indicates that the reaction with the acidic melt is complete.

2. Electrochemistry of Mo Dimers

A manuscript, "Electrochemistry of Molybdenum Chloride Dimers in a Basic Ambient Temperature Molten Salt", has been published in Inorganic Chemistry. See Appendix A, Ref. 89.

ABSTRACT

The Mo(III) dimers, $\text{Mo}_2\text{Cl}_9^{3-}$ and $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ and the molybdenum(II) dimer $\text{Mo}_2\text{Cl}_8^{4-}$, have been studied in the basic ambient-temperature molten salt AlCl_3 -1-methyl-3-ethylimidazolium chloride (ImCl) by employing electrochemistry and visible spectroscopy. Both Mo(III) dimers are reduced to the Mo(II) dimer at approximately the same potential in a single, irreversible two-electron step. The quadruply bonded dimer, $\text{Mo}_2\text{Cl}_8^{4-}$, undergoes a quasi-reversible, one-electron oxidation to $\text{Mo}_2\text{Cl}_8^{3-}$ and is further oxidized to $\text{Mo}_2\text{Cl}_9^{3-}$ in an irreversible, one-electron step at more anodic potentials. The hydride dimer $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ undergoes an irreversible, two electron oxidation that produces $\text{Mo}_2\text{Cl}_9^{3-}$ and a proton. The electrochemical and chemical interconversions of the dimers are summarized as follows:



3. Reaction of Protons with Mo Dimers

A manuscript, "Reactions of Protons and Molybdenum Dimers in an Ambient Temperature Molten Salt", has been published in Inorganic Chemistry. See Appendix A, Ref. 92.

SUMMARY

The interaction between $\text{Mo}_2\text{Cl}_8^{4-}$ with proton, to yield the hydrido-bridged Mo(III) dimer, $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ was examined in some detail. The hydrido ligand reacts with EtAlCl_2 , which removes protonic impurities from the melt, to regenerate the octachloro Mo(II) complex. The addition of excess EtAlCl_2 makes possible the direct addition of $\text{Mo}_2(\text{acetate})_4$ to a basic melt to generate the $\text{Mo}_2\text{Cl}_8^{4-}$ dimer. The excess of EtAlCl_2 does not interfere with an examination of the electrochemistry of the $\text{Mo}_2\text{Cl}_8^{4-}$ in the melt.

4. Examination of Melt Voltage Limits at Microelectrodes

A manuscript, "Microelectrodes in the Examination of Anodic and Cathodic Limit Reactions of an Ambient Temperature Molten Salt", has been published in the Journal of Electroanalytical and Interfacial Chemistry. See Appendix A, Ref. 93.

ABSTRACT

Tungsten microelectrodes of 25 μm radius have been employed to examine the cathodic and anodic limits of the 0.8:1.0 $\text{AlCl}_3 + \text{ImCl}$ ambient temperature molten salt, where ImCl is 1-methyl-3-ethylimidazolium chloride. Staircase cyclic voltammetric scans were performed well beyond the normal electrochemical potential limits. In the cathodic region, reduction of Im^+ was seen clearly at -2.3 V, and another unknown reduction process at -5.5 V was also observed. In the anodic region, oxidation of both Cl^- at 1.3 V and AlCl_4^- at 3.0 V were observed. From normal pulse voltammetry, diffusion coefficients for Im^+ and Cl^- were determined to be $(1.02 \pm 0.03) \times 10^{-7} \text{ cm}^2/\text{s}$ and $(6.1 \pm 1.0) \times 10^{-7} \text{ cm}^2/\text{s}$, respectively.

5. Aluminum Anodization

A manuscript, "Aluminum Anodization in Basic Ambient Temperature Molten Salts", was published in the Journal of the Electrochemical Society. See Appendix A, Ref. 98. This work was also partially supported by the S.D.I.O/I.S.T and managed by the Office of Naval Research.

ABSTRACT

Aluminum anodization has been studied in the basic AlCl_3 -1-methyl-3-ethylimidazolium chloride (ImCl) ambient temperature molten salt ($\text{AlCl}_3:\text{ImCl}$ molar ratio < 1.0). The anodization process was studied as a function of chloride anion concentration. Two different anodization processes are observed with onset potentials of approximately -1.1 and 0 V. The more cathodic anodization involves formation of the tetra-

chloroaluminate anion and exhibits a limiting current controlled by diffusion of chloride to the electrode surface. The number of chlorides required for each Al anodized was determined to be 4.6 ± 0.4 . The more anodic anodization shows no diffusion control. A value for the diffusion coefficient of chloride was obtained which is lower than previously reported; the difference involves using an n value of 1, rather than $2/3$. No reduction of the tetrachloroaluminate anion was observed even at elevated temperatures.

6. Study of the Ferro/Ferricyanide Couple

A manuscript, "The Ferro/Ferricyanide Couple in Aluminum Chloride-Imidazolium Chloride Ambient Temperature Molten Salts", has been published in Inorganic Chemistry. See Appendix A, Ref. 96.

ABSTRACT

Tetrabutylammonium ferricyanide, $(\text{Bu}_4\text{N})_3\text{Fe}(\text{CN})_6$, has been prepared and investigated in the 1-methyl-3-ethylimidazolium chloride-aluminum chloride (ImCl-AlCl_3) ambient-temperature molten salt solvent. The voltammetry and UV-visible spectroscopy of $(\text{Bu}_4\text{N})_3\text{Fe}(\text{CN})_6$ have been compared to those of $\text{K}_3\text{Fe}(\text{CN})_6$ in water and are shown to be identical; in addition, the molecular weight of $(\text{Bu}_4\text{N})_3\text{Fe}(\text{CN})_6$ has been determined by an electroanalytical method and is in good agreement with that expected. $(\text{Bu}_4\text{N})_3\text{Fe}(\text{CN})_6$ is insoluble in the basic ImCl-AlCl_3 melt but is soluble in the acidic melt. However, the ferricyanide reacts to form the ferrocyanide species; i.e., the oxidation potential of the ferro/ferricyanide couple is sufficiently positive to oxidize chloride from tetrachloroaluminate. Spectral shifts observed for the molten salt suggest that AlCl_3 forms adducts with the ferrocyanide, which accounts for the large positive shift in the oxidation potential of the ferro/ferricyanide redox couple relative to that in water. The ferro/ferricyanide couple could be examined voltammetrically at a carbon, but not a platinum, electrode since the tetrachloroaluminate oxidation is significantly more irreversible on the former than the latter, and the formal potential was estimated as $+2.30$ V vs an Al reference in the 1.5:1 molten salt.

7. Ferrocene Electrochemistry

Some preliminary work was initiated to measure the kinetics of the ferrocene/ferrocenium couple in the ImCl-AlCl_3 melt. Cyclic voltammetry at Pt ultramicroelectrodes was carried out in which background subtraction of charging currents was performed; the electron transfer kinetics were found to be surprisingly slow. However, normal pulse voltammetric measurements were also carried out, and the kinetic analysis disagreed with that of the cyclic voltammetry. Experimental problems were encountered, as this work was carried out during our initial efforts to perform ultramicroelectrode work in the molten salts (F. Uribe and R. A. Osteryoung, unpublished). We plan to continue this work under our new AFOSR grant.

C. NON-ELECTROCHEMICAL STUDIES

1. Oxide Species in ImCl-AlCl_3 .

Two manuscripts on this topic, with some redundancy, have been published. The first, "Aspects of the Chemistry of Water in Ambient Temperature Chloroaluminate Ionic Liquids: ^{17}O NMR Studies", was published in Inorganic Chemistry. See Appendix A, Ref. 82. The second, "The Chemistry of Water in Ambient Temperature Chloroaluminate Ionic Liquids: NMR Studies" was published in the Proceedings of the Joint International Symposium on Molten Salts. See Appendix A., Ref. 83.

SUMMARY

^{17}O enriched water was added to the ambient temperature molten salt to study the behavior of oxide species in the melts. In the acidic melts, three ^{17}O lines which varied in intensity but not in position as the melt composition was changed, indicated that three oxide species in slow exchange were present. In the basic melt, only one ^{17}O line was observed; the position varied with melt composition. It was concluded that there are probably two species, one in rapid exchange, in the basic melt. As a result of experiments in which HCl was bubbled through the melt and the spectra examined, one of the species in both the acidic and basic melts is believed to be protonated.

2. Pyrrole Adduct Formation

A manuscript, "On the Chemistry of Pyrrole in Room Temperature Chloroaluminate Melts", has been published in the Journal of Electroanalytical and Interfacial Chemistry. See Appendix A, Ref. 95.

ABSTRACT

The chemistry of pyrrole in room-temperature molten salts composed of mixtures of AlCl_3 with 1-methyl-3-ethylimidazolium chloride has been studied by ^1H - and ^{13}C -NMR spectroscopy. The spectra indicate that an adduct is formed between pyrrole and AlCl_3 in melts containing an excess of AlCl_3 ; no adduct formation occurs in melts containing excess organic chloride. The structure of the adduct is deduced and used to explain the previously observed inability to polymerize pyrrole electrochemically in acidic melts.

3. Proton Removal from Molten Salts

A manuscript, "Removal of Protons from Chloroaluminate Ionic Liquids", has been published in Analytical Chemistry. See Appendix A, Ref. 84.

SUMMARY

EtAlCl_2 added to the molten salt removes protons. Normal pulse voltammetric studies, in which the proton reduction wave was monitored as EtAlCl_2 was added to the melt, indicated quantitative removal of proton in a 1:1 ratio with added EtAlCl_2 . NMR results supported the quantitative removal of proton.

4. Preparation of a New Molten Salt, ImHCl_2

A manuscript, "1-Methyl-3-Ethylimidazolium Hydrogen Dichloride: Synthesis and Application to the Study of Protons in Ambient Temperature Chloroaluminate Ionic Liquids", has been published in Inorganic Chemistry. See Appendix A, Ref. 94.

ABSTRACT

The synthesis of 1-methyl-3-ethylimidazolium hydrogen dichloride (ImHCl_2) and its deuterium analog, (Im^2HCl_2), and their use as proton/deuterium donors in ambient-temperature chloroaluminate melts are described. The material exists as a liquid at room temperature and has been characterized by ^1H spectroscopy. ImHCl_2 is itself an ambient-temperature molten salt composed of the Im^+ cation and HCl_2^- anion. The ^2H NMR chemical shifts of species derived from ImDCl_2 in 1-methyl-3-ethylimidazolium chloride/aluminum chloride melts lead us to suggest that HCl interacts with a second chloride in basic melts, whereas it is more weakly complexed in acidic melt solutions. The quantitative addition of proton by ImHCl_2 is demonstrated by use of pulse voltammetry.

5. Oxide and Hydroxide Species in the Molten Salts

A manuscript, "Oxide and Hydroxide Species Formed on Addition of Water to Ambient Temperature Chloroaluminate Melts: An ^{17}O NMR Study", has been submitted to Inorganic Chemistry. See Appendix A, Ref. 100.

ABSTRACT

The variation of the intensity of ^{17}O NMR lines with manipulation of proton concentration and melt composition has been used to model oxy- and hydroxy-chloroaluminate species in the ambient temperature molten salt system, 1-methyl-3-ethylimidazolium chloride:aluminum chloride. It is concluded that the most probable oxy-chloroaluminate species in acidic melts are $\text{Al}_3\text{OCl}_8^-$ and either $\text{Al}_3\text{O}_2\text{Cl}_6^-$ or $\text{Al}_2\text{OCl}_5^-$ and the most probable hydroxy-chloroaluminate species are $\text{Al}_3\text{Cl}_9\text{OH}^-$ or $\text{Al}_2\text{Cl}_6\text{OH}^-$, with the latter being favored. In the basic melts, the most probable oxy- and hydroxy-chloroaluminate species are $\text{Al}_2\text{OCl}_5^-$ and $\text{Al}_2\text{Cl}_6\text{OH}^-$.

6. Gutmann Donor-Acceptor Numbers

A manuscript, "Donor-Acceptor Properties of Ambient Temperature Chloroaluminate Melts", has been published in Inorganic

Chemistry. See Appendix A, Ref. 99.

ABSTRACT

The donor-acceptor properties of room-temperature chloroaluminate ionic liquids composed of mixtures of AlCl_3 with either N-(1-butyl)pyridinium chloride or 1-methyl-3-ethylimidazolium chloride were studied. Gutmann donor and acceptor numbers were determined by using the Eu(III) reduction potential and the ^{31}P chemical shift of triethylphosphine oxide, respectively. Acidic melts are extremely poor donor and strong acceptor media. Basic melts are similar in basicity to DMF. No conclusions concerning the acceptor properties of the basic melt are drawn from this work since the strongly basic probe molecule, $\text{Et}_3\text{P}=\text{O}$, is leveled by the solvent. Conditions under which these parameters are potentially useful are outlined.

D. ULTRAMICROELECTRODES

To make use of ultramicroelectrodes in the molten salts, we felt it necessary to carry out work under less difficult experimental conditions to establish criteria for using these electrodes when carrying out pulse voltammetry. The two papers below result from this work.

1. Normal and Reverse Pulse Voltammetry at Microdisk Electrodes

A manuscript, "Normal and Reverse Pulse Voltammetry at Microdisc Electrodes", was published in Analytical Chemistry. See Appendix A, Ref. 90.

ABSTRACT

Normal and reverse pulse voltammetry have been carried out on stationary microdisk electrodes where nonplanar diffusion can be significant. Boundary conditions are shown to be readily renewed for both normal and reverse pulse modes by simply waiting for fixed periods of time between pulses. The superposition theorem is shown to be applicable even under conditions where substantial nonplanar diffusion is present. An equation permitting the estimate of the error in the normal pulse limiting current for ratios of pulse width to waiting time for renewal of boundary conditions is presented.

2. Normal and Reverse Pulse Voltammetry from Poised Systems

A manuscript, "Normal and Reverse Pulse Voltammetry from Poised Systems at Microdisk Electrodes" has been published in Analytical Chemistry. See Appendix A, Ref. 91.

ABSTRACT

Normal and reverse pulse voltammetry have been carried out

at microdisk electrodes under conditions where the electrode is effectively in a poised medium. This is accomplished by initiating the experiments from a potential so that the surface concentrations of the oxidized and reduced species, ferri- and ferrocyanide, are both finite. Agreement between theory and experiment is shown to be excellent.

II. WORK IN PROGRESS

We here briefly discuss work ongoing at the completion of this current grant. A good deal of this was a part of our new proposal submitted to A.F.O.S.R. and will be continued under the new project.

A. STUDIES OF MODIFIED ELECTRODES

We are initiating work to study polyaniline in the molten salts; we found that aniline could be polymerized in the neutral melt, and that polyaniline shows electroactivity, but have done not studied this potentially useful reaction.

B. STOICHIOMETRY OF METAL COMPLEXES

Work is in progress to determine the stoichiometry of metal chlorocomplexes in neutral melts by amperometric titrations. A manuscript based on this will be submitted for publication.

C. FERROCENCE KINETICS

As described previously, we started this work some time ago; it is our intention to resume this study making use of ultramicroelectrodes.

D. SUPERACID CHEMISTRY/ELECTROCHEMISTRY

The addition of proton to the acidic Lewis acid molten salt system results in a superacid. We have embarked upon studying the interaction of protons with a variety of solutes, making use of ^1H , ^2H , and ^{13}C NMR, and electrochemistry. This topic was a major part of our new proposal to A.F.O.S.R. and will be continued.

III. INTERACTION WITH AIR FORCE LABORATORIES AND PERSONNEL

Interactions, either via the telephone or at various meetings, with Frank J. Seiler Research Laboratory personnel have continued during the life of this grant. An Molten Salt Contractors meeting was held at the Frank J. Seiler Research Laboratory in April, 1987, and a Contractors meeting was again held in Gatlinburg, Tennessee in October 1988.

IV. OTHER ACTIVITIES

The Principal Investigator was awarded the C. N. Reilley Award in Electroanalytical Chemistry; the award is sponsored by the Society of Electroanalytical Chemistry, and was presented at the Pittsburgh Conference of Analytical Chemistry and Applied Spectroscopy in March, 1987. A Short Course consisting of 10 lectures on "Molten Salt Electrochemistry" was given at the University of the Andes, Mérida, Venezuela, in June - July of 1989.

VI. PERSONNEL

Personnel associated with this grant for any extended period of time during the grant period are listed below.

Senior Research Personnel

Dr. Laura Janiszewska
Dr. Jean Francois Oudard
Dr. Francisco Uribe
Dr. Basudev Das
Dr. Soo-Gil Park
Dr. John O'Dea
Dr. Richard Carlin
Mr. Sinru Lin*

Junior Research Personnel

Mr. Thomas A. Zawodzinski, Jr.**
Mr. Marc A-M. Noel
Capt. Paul Trulove*

* Not paid on Grant funds

** Ph.D. received, June, 1989

APPENDIX A

Publications--Grant Related Activity - since AFOSR support initiated.

AFOSR-71-1955; 1 Jan. 1971 - 28 Feb. 1975

1. Janet Osteryoung and R. A. Osteryoung, "The Advantage of Charge Measurements for Determining Kinetic Parameters", *Electrochimica Acta*, 16, 525 (1971).
2. R. A. Osteryoung, "Introduction to the On-Line Use of Computers in Electrochemistry", Vol. II, "Application of Computers to Chemical Instrumentation", Ed. by Mattson, Mark and MacDonald, Marcel Dekker (1973).
3. L. G. Boxall, H. L. Jones and R. A. Osteryoung, "Solvent Equilibria in AlCl₃-NaCl Melts", *J. Electrochem. Soc.*, 120(2), 223 (1973).
4. H. Lloyd Jones, L. G. Boxall and R. A. Osteryoung, "Organic Electrode Reactions in Fused AlCl₃ Containing Solvents", *J. Electroanal. Chem.*, 38, 476 (1972).
5. L. G. Boxall, H. L. Jones and R. A. Osteryoung, "Electrochemical Studies on Ag, Fe and Cu Species in AlCl₃-NaCl Melts", *J. Electroanal. Chem.*, 121, 212 (1974).
6. H. Lloyd Jones and R. A. Osteryoung, "Electrode Reactions of Aromatic Amines in Solvents Containing Fused AlCl₃, II.", *J. Electroanal. Chem.*, 49, 281 (1974).
7. R. J. Gale and R. A. Osteryoung, "Investigation of Subvalent Ion Effects During Aluminum Anodization in Molten NaCl-AlCl₃ Solvents", *J. Electrochem. Soc.*, 121, 983 (1974).
8. V. R. Koch, L. L. Miller and R. A. Osteryoung, "Reductive Defunctionalization of 1-substituted Adamantanes in Molten Sodium Tetrachloroaluminate", *J. Org. Chem.*, 39, 2416 (1974).
9. H. Lloyd Jones and R. A. Osteryoung, "Organic Reactions in Molten Tetrachloroaluminate Solvents", *Advances in Molten Salt Chemistry*, Vol. 3, Edited by J. Braunstein, G. P. Smith and G. Mamantov, Plenum Publishing (1975).
10. R. J. Gale and R. A. Osteryoung, "Dissociative Chlorination of Nitrogen Oxides and Oxyanions in Molten Sodium Chloride-Aluminum Chloride Solvent", *Inorg. Chem.*, 14, 1232 (1975).
11. H. L. Chum, V. R. Koch, L. L. Miller and R. A. Osteryoung, "An Electrochemical Scrutiny of Organometallic Iron Complexes and Hexamethylbenzene in a Room Temperature Molten Salt", *J. Am. Chem. Soc.*, 97, 3264 (1975).
12. D.E. Bartak and R. A. Osteryoung, "The Electrochemical Oxidation of N,N,N',N'-Tetramethylbenzidine in Molten Sodium Tetrachloroaluminate", *J. Electrochem. Soc.*, 122, 600 (1975).

13. J. Phillips, R. J. Gale, R. G. Wier and R. A. Osteryoung, "Glassy Carbon Rotating Ring-Disc Electrodes for Molten Salt Studies", *Anal. Chem.*, 48, 1266 (1976).
14. D. E. Bartak and R. A. Osteryoung, "The Redox Behavior of Tetrachloro-p-Benzoquinone-Tetrachlorohydroquinone Systems in Molten Aluminum Chloride-Sodium Chloride Solvents", *J. Electroanal. Chem.*, 74, 69 (1976).

AFOSR 75-2776; 1 March 1975 - 31 May 1976

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Meeting Presentation and Seminars--Related to Grant Activity

(*Invited Presentations)

1971

*R. A. Osteryoung, "Computerized Electrochemical Experimentation", Department of Chemistry Colloquia, Pennsylvania State University, University Park, PA, May 27, 1971.

*L. G. Boxall, H. L. Jones and R. A. Osteryoung, "Electrochemical Studies in Aluminum Chloride Melts", N. W. Regional ACS Meeting, Bozeman, Montana, June, 1971.

*R. A. Osteryoung, "Application of a Computer-Based Pulse Polarographic System in Molten Salt Studies", Gordon Research Conference on Molten Salts, Kimball Union Academy, Meriden, N.H., August, 1971.

*R. A. Osteryoung, "Use of a Mini-Computer in Electrochemical Studies", Symposium on Mini-Computers in the Research & Teaching Laboratory, American Chemical Society Meeting, Washington, D.C., September, 1971.

1972

*R. A. Osteryoung, "Chemistry and Electrochemistry in Fused Salts", Baylor University (ACS Waco Section) May 8, 1972.

*R. A. Osteryoung, "Computer Controlled Electrochemical Experimentation", Texas Christian University (Dallas-Fort Worth ACS Section) May 9, 1972.

*R. A. Osteryoung, "Computer Controlled Electrochemical Experimentation", (San Antonio, Texas ACS Section) May 10, 1972.

*R. A. Osteryoung, "Computer Controlled Electrochemical Experimentation", Texas A&M (College Station, Texas ACS Section) May 11, 1972.

*R. A. Osteryoung, "Computer Controlled Electrochemical Experimentation", Midwestern University (Wichita Falls, Texas/Duncan, Oklahoma ACS Section), May 12, 1972.

*H. L. Jones, L. G. Boxall and R. A. Osteryoung, "Organic Electrochemistry in Aluminum Halide Melts", Rocky Mountain Regional ACS Meeting, Ft. Collins, CO, June 1972.

1973

*R. A. Osteryoung, H. L. Jones and L. G. Boxall, "Electrochemical Studies in Molten Chloroaluminates", Symposium on Fused Salt Technology, Electrochemical Society Meeting, Chicago, May 8-13, 1973.

*R. A. Osteryoung, R. H. Abel, L. G. Boxall and B. H. Vassos, "An Introduction to the On-Line Use of Digital Computers in Electrochemistry", Plenary Lecture at Symposium on Electrochemical Measurements by Digital Computer, Electrochemical Society Meeting, Chicago, May 8-13, 1973.

1974

D. E. Bartak and R. A. Osteryoung, "Oxidation of Tetramethylbenzidine in Chloroaluminate Melts", Electrochemical Society, San Francisco, CA, May 1974.

*R. A. Osteryoung, "Chemistry in Aluminum Chloride Melts", Fifth International Conference in Non-Aqueous Solutions, International Union of Pure and Applied Chemistry, Vienna, July 10-12, 1974.

*R. A. Osteryoung, "Electrochemical Studies in Fused Salts", First Latin American Electrochemistry and Corrosion Meeting (ABRACO), Rio de Janeiro, Brazil, October 21-25, 1974.

1975

*R. A. Osteryoung, "Some Applications of Pulse Techniques to Analytical Chemistry and Electrochemistry", University of Brussels, Brussels, Belgium, March 17, 1975.

V. R. Koch, L. L. Miller and R. A. Osteryoung, "Electroinitiated Fiedel-Crafts Transalkylation in a Room Temperature Molten Salt Medium", Mile High Electrochemistry Symposium, Colorado Electrochemical Society Section, Fort Collins, CO, May 3, 1975.

K. A. Paulsen and R. A. Osteryoung, "Electrochemical Studies of Sulfur in Molten Sodium Tetrachloroaluminate", Fall Meeting, American Chemical Society, Chicago, Illinois, August 1975.

*R. A. Osteryoung, "Electrochemical Studies in Molten Sodium Chloride-Aluminum Chloride", Colorado College, Colorado Springs, Colorado, December 4, 1975.

1976

*R. A. Osteryoung, "Chemical and Electrochemistry in Aluminum Chloride Molten Salt Systems", International Symposium on Molten Salts, Spring Meeting, The Electrochemical Society, Washington, D.C., May 2-7, 1976.

*R. A. Osteryoung, "Electrochemical Studies in Molten Chloroaluminates", Gould, Inc., Rolling Meadows, Illinois, May 4, 1976.

*R. A. Osteryoung, "Chemical and Electrochemical Studies in Molten Chloroaluminate Solvents", Department of Chemistry Colloquium, Purdue University, West Lafayette, Indiana, March 23, 1976.

*R. A. Osteryoung, "Acid-Base Dependent Electrochemistry in Aluminum Halide Molten Salts", Gordon Research Conference on Molten Salts and Metals, Tilton, N.H., July 24-29, 1977.

*R. A. Osteryoung, "Chemistry and Electrochemistry in Molten Chloroaluminates", Georgia Institute of Technology, Atlanta, GA, October 12, 1977.

*J. Robinson and R. A. Osteryoung, "The Electrochemistry of Selenium in Molten Sodium Tetrachloroaluminates", 3rd Annual Mile High Symposium on Electrochemistry, Rocky Mountain Section of the Electrochemical Society, Fort Collins, CO, May 7, 1977.

1978

*R. A. Osteryoung, "Chemistry and Electrochemistry in Molten Chloroaluminates", Georgetown University, Washington, D.C., February 9, 1978.

R. A. Osteryoung and B. Gilbert, "Electrochemistry of Nickel in Molten Sodium Tetrachloroaluminates", National American Chemical Society Meeting, Anaheim, CA, March 12-17, 1978.

*R. A. Osteryoung, "Chemistry and Electrochemistry in Molten Chloroaluminates", Wichita State University, Wichita, KS (April, 1978).

*R. A. Osteryoung, "Electrochemistry in Molten Chloroaluminates", Naval Surface Weapons Center, White Oak, Maryland (May, 1978).

*R. A. Osteryoung, "Acid Base Dependent Electrochemistry in Chloroaluminate Melts", Conference on Highly Concentrated Aqueous Solutions and Molten Salts, Oxford University, Oxford, England (July 5-7, 1978).

*R. A. Osteryoung, "Acid Base Dependent Chemistry and Electrochemistry in Chloroaluminate Melts", The University of Southampton, Southampton, England (July 10, 1978).

*R. A. Osteryoung, R. J. Gale, J. Robinson, R. Bugle and B. Gilbert, "Electrochemical Studies in a Room Temperature Molten Salt", Second International Meeting on Molten Salts, The Electrochemical Society, Pittsburgh, PA (October 15-20, 1978).

*R. A. Osteryoung, "Acid-Base Dependent Chemistry and Electrochemistry in Molten Chloroaluminates", Gould, Inc., Rolling Meadows, IL, November 16, 1978.

*R. A. Osteryoung, "Acid-Base Dependent Chemistry and Electrochemistry in Molten Chloroaluminates", Colorado Section, American Chemical Society, University of Colorado, December 12, 1978 (Colorado Section Award Talk).

1979

*R. A. Osteryoung, "Room Temperature Molten Salts: A New Class of Solvents" Gordon Research Conference on Electrochemistry, Santa Barbara, CA, January 7-12, 1979.

*R. A. Osteryoung, "Studies in Molten Chloroaluminates", Oak Ridge National Laboratory, Oak Ridge, TN, February 2, 1979.

*R. A. Osteryoung, J. Robinson and R. J. Gale, "Oxidation of Aromatic Hydrocarbons in a Room Temperature Molten Salt", Symposium on Electrochemistry and Spectroscopy in Melts, American Chemical Society/Chemical Society of Japan Congress, Honolulu, Hawaii, April 1-6, 1979.

James Robinson and R. A. Osteryoung, "Electrochemical Studies on Some Aromatic Amines in a Room Temperature Molten Salt", Spring Meeting, The Electrochemical Society, St. Louis, MO, May 11-16, 1979.

*R. J. Gale, A. J. Nozik and R. A. Osteryoung, "Electrochemical Characterization of the Semiconductor TiO_2 -Room Temperatures Molten Salt Interface", Rocky Mountain Regional Electrochemical Society Meeting, Ft. Collins, CO (June, 1979).

*G. Cheek and R. A. Osteryoung, "Electrochemical and Infrared Studies of Quinones in a Room Temperature Molten Salt", Gordon Research Conference on Molten Salt", Gordon Research Conference on Molten Salts and Metals, Brewster Academy, Wolfeboro, New Hampshire (August 20-24, 1979).

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*R. A. Osteryoung, "Ambient Temperature Molten Salts - A New Class of Solvents", Penn-York American Society Section, Jamestown, New York November 7, 1983 (ACS Tour Speaker).

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*R. A. Osteryoung, "Aspects of Ambient Temperature Molten Salts", Molten Salt Discussion Group, London, England, December 16, 1985.

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*R. A. Osteryoung, "Ambient Temperature Molten Salts; A New Class of Solvents", Department of Chemistry, University of Florida, Gainesville, FL, March 3, 1987 (ACS Tour Speaker).

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*Paul Trulove, Richard Carlin, Soo-Gill Park and R. A. Osteryoung, "Interaction of Protons with Organic Bases in Ambient Temperature Molten Salts", Electrochemistry Symposium, Rocky Mountain Regional American Chemical Society Meeting, Denver, CO, July 30 - August 4, 1989.

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COMPLETED PROJECT SUMMARY

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PRINCIPAL INVESTIGATOR: Dr. Robert Osteryoung
Department of Chemistry
State University of New York
Buffalo, NY 14214

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SENIOR RESEARCH PERSONNEL

Dr. Richard Carlin
Dr. Basudev Das
Dr. Laura Janiszewska
Dr. John O'Dea
Dr. Jean Francois Oudard
Dr. Soo-Gil Park
Dr. Francisco Uribe

Prof. Robert Allendoerfer*
Prof. Janet Osteryoung*

JUNIOR RESEARCH PERSONNEL:

Mr. Sinru Lin*
Mr. Marc A-M. Noel
Capt. Paul Trulove*
Mr. Thomas Zawodzinski, Jr.**

* Not paid on Grant funds

** Ph.D. received, June, 1989

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"Electrochemistry of Polythiophene and Polybithiophene Films in Ambient Temperature Molten Salts", L. Janiszewska and R. A. Osteryoung, J. Electrochem. Soc., 134, 2787 (1987).*

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The objective of work carried out under this grant was to perform chemical and electrochemical studies in an ionic liquid, a mixture of aluminum chloride with 1-ethyl-3-methylimidazolium chloride. Work carried out is divided into the areas of a) studies of modified, electroactive polymer coated electrodes; b) electrochemical studies of solutes; c) non-electrochemical studies, primarily involving NMR studies of solutes in the ionic liquids; d) the use of ultramicroelectrodes.

In the electroactive polymer area, simultaneous EPR and electrochemical studies on polypyrrole and polyfluorene were carried out. A strong correlation between the maximum EPR absorbance and cyclic voltammetric peak currents was shown to exist. The polymerization of fluorene to form polyfluorene was examined; the film was conductive in the oxidized state and nonconductive when reduced. However, residual EPR signals were found in apparently fully oxidized and fully reduced polyfluorene, although, as was the case with polypyrrole, correlation of the maximum in the EPR signal with peak currents in cyclic voltammetry could be made.

In the solute electrochemical area, the behavior of 1,4-benzoquinone was studied; fast scan voltammetry at ultramicroelectrodes indicated a fast two-electron step, probably followed by dianion solvation. The electrochemistry of two Mo(III) dimers, $\text{Mo}_2\text{Cl}_9^{3-}$ and $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ and the molybdenum(II) dimer $\text{Mo}_2\text{Cl}_8^{4-}$, were studied in the basic ambient-temperature molten salt and the mechanistic pathways determined. In addition, the interaction between $\text{Mo}_2\text{Cl}_8^{4-}$ with proton, to yield the hydrido-bridged Mo(III) dimer, $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ was examined in some detail. In another piece of work, aluminum anodization was examined in the basic

melt. Two different anodization processes were observed, one involves formation of the tetrachloroaluminate anion and exhibits a limiting current controlled by diffusion of chloride to the electrode surface while the other anodization shows no diffusion control. However, no reduction of the tetrachloroaluminate anion was observed even at elevated temperatures. In another study, $(\text{Bu}_4\text{N})_3\text{Fe}(\text{CN})_6$ was prepared and the ferro/ferricyanide couple was investigated in the acidic molten salt. However, the ferricyanide reacts to form the ferrocyanide species; i.e., the oxidation potential of the ferro/ferricyanide couple was sufficiently positive to oxidize chloride from tetrachloroaluminate. The ferro/ferricyanide couple could, however, be examined voltammetrically at a carbon, but not a platinum, electrode since the tetrachloroaluminate oxidation is significantly more irreversible on the former than the latter.

NMR spectroscopy was employed in several studies. ^{17}O enriched water was added to the ambient temperature molten salts to study the behavior of oxide species in the melts. In the acidic melts, three ^{17}O lines were observed which varied in intensity but not in position as the melt composition was changed. In the basic melt, only one ^{17}O line was observed; the position varied with melt composition. HCl was bubbled through the melt and the spectral changes examined; it was concluded that one of the species in both the acidic and basic melts was a protonated $-\text{Al}-\text{O}-\text{H}$ entity. In another piece of work, the chemistry of pyrrole in the melt was examined by ^1H - and ^{13}C -NMR spectroscopy. The spectra indicate that an adduct is formed between pyrrole and AlCl_3 in melts containing an excess of AlCl_3 ; no adduct formation occurs in melts containing excess organic chloride. The Gutmann donor-acceptor properties of acidic and basic melts were determined by using the $\text{Eu}(\text{III})$ reduction potential and the ^{31}P chemical shift of triethylphosphine oxide, respectively. Acidic melts are extremely poor donor and strong acceptor media. Basic melts are similar in basicity to DMF.

Two pieces of work related to proton addition and removal were carried out. EtAlCl_2 added to the molten salt was found to remove protons. Normal pulse voltammetric studies, in which the proton reduction wave was monitored as EtAlCl_2 was added to the melt, indicated quantitative removal of proton in a 1:1 ratio with added EtAlCl_2 . 1-methyl-3-ethylimidazolium hydrogen dichloride (ImHCl_2) and its deuterium analog, (Im^2HCl_2), were synthesized and used as proton/deuterium donors in the molten salts. ImHCl_2 is itself an ambient-temperature molten salt composed of the Im^+ cation and HCl_2^- anion. The quantitative addition of proton by ImHCl_2 was demonstrated by use of pulse voltammetry.

Microelectrodes were employed in several studies. Tungsten microelectrodes of 25 μm radius were employed to examine the cathodic and anodic limits of the basic melt, and staircase cyclic voltammetric scans were performed well beyond the normal electrochemical potential limits. To learn more about the use of microdisk electrodes, normal and reverse pulse voltammetry was carried out on stationary microdisk electrodes in aqueous solutions in both poised and unpoised systems. The systems were poised by initiating the experiments from a potential so that the surface concentrations of the oxidized and reduced species, ferri- and

ferrocyanide, are both finite. Boundary conditions are shown to be readily renewed for both normal and reverse pulse modes by simply waiting for fixed periods of time between pulses. The superposition theorem was shown to be applicable even under conditions where substantial nonplanar diffusion was present. An equation permitting the estimate of the error in the normal pulse limiting current for ratios of pulse width to waiting time for renewal of boundary conditions was presented.

AFOSR PROGRAM MANAGER: Dr. John Wilkes